

Title	Reaction of Di- μ -chlorobis {2-[1- η^5 - Cp] } dipalladium with Halogens : A Possible Involvement of Pd (IV) Intermediate (Commemoration Issue Dedicated to Professor Shinzaburo OKA On the Occasion of His Retirement)
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Reaction of Di- μ -chlorobis{2-[1-(chloromethyl)vinyl]- π allyl}dipalladium with Halogens. A Possible Involvement of Pd(IV) Intermediate

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Di- μ -chlorobis{2-[1-(chloromethyl)vinyl] π allyl}dipalladium undergoes reaction with iodine monochloride, iodine monobromide and bromine to yield tetrakis(halomethyl)ethylene derivatives in almost quantitative yields.

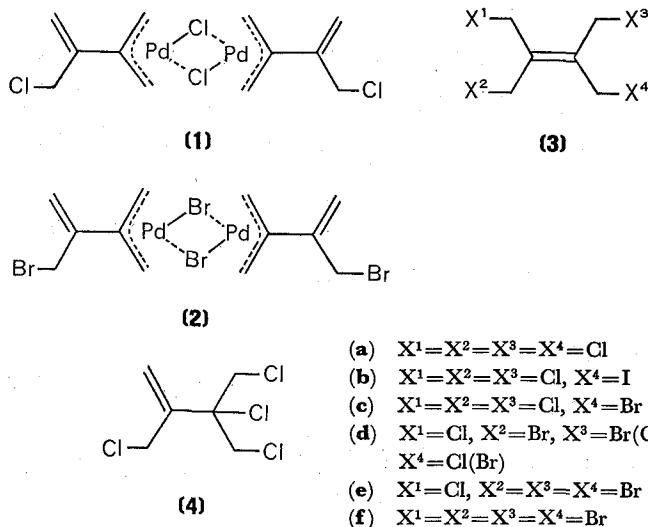
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2, 3-Bis(bromomethyl)-1, 3-butadiene is a versatile reactive synthetic intermediate.¹⁾ The potential of this intermediate can be envisaged by its use for many efficient synthesis of different classes of compounds.¹⁻⁴⁾ Of the few methodologies reported for the preparation of 2, 3-bis(bromomethyl)-1, 3-butadiene, zinc-copper couple induced debromination of tetrakis(bromomethyl)ethylene (**3f**) seems most practical.²⁾ Although the methodologies for the synthesis of **3f** are sporadically described in the literature,⁵⁻⁷⁾ little attention has been focussed on the related compounds with different halogens (**3b-e**). To the best of our knowledge, there is only one report⁸⁾ which describes the preparation of such compounds by the addition of halogens to the suitably substituted 1, 3-butadienes and no further work has been undertaken. Recently we have reported⁹⁾ the high yield synthesis of **3f** and 2, 3-bis(bromomethyl)-1, 3-butadiene by the reaction of bromine with di- μ -bromobis{2-[1-(bromomethyl)vinyl] π allyl}dipalladium (**2**). In continuation of this work, we have now investigated the reaction of di- μ -chlorobis{2-[1-(chloromethyl)vinyl] π allyl} dipalladium (**1**) with iodine monochloride, iodine monobromide and bromine in an attempt to develop a new approach to the tetrakis(halomethyl)ethylene derivatives (**3**). The results are summarized in Table I.

The dependence of the reaction on the amount of halogen used was examined initially by carrying out the reactions in the 1:1, 1:2 and 1:10 molar ratios of the substrate to halogen. The best yields of the desired products (**3**) were obtained when the substrate and halogen were taken in the 1:10 molar ratio. In the runs with 1:1 and 1:2 molar ratios, though no starting material left unreacted, large amount of undesired products, organopalladium complexes, were obtained which

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Table 1. Reaction of **1** with Halogens^{a)}

Run	X ₂	1/Reag. Molar ratio	Total yield ^{b)} (%)	Distribution ^{c)}	¹ H-NMR, δ (in CDCl ₃) ^{d)}
1	ICl	1:10	79	3a (11) 3b (31) 4 (100)	4.072 (s, 75.3 ^{e)} , $\text{Cl-CH}_2\text{-Cl}$, 4.275 (s, 40.3, $=\text{CCH}_2\text{Cl}$), 5.222 and 5.730 (d each, J=2Hz, 36.9, $\text{C}=\text{CH}_2$)
2	IBr	1:10	89	3c (30) 3d (68) 3e (100) 3f (36)	4.139 (s, 27.6, $=\text{CCH}_2\text{Br}$), 4.242 (s, 13.4, $=\text{CCH}_2\text{Cl}$)
3	Br ₂	1:10	85	3a (7) [30] ^{f)} 3c (63) [89] 3d (100) [100] 3e (81) [87] 3f (33) [50] (116) [14] ^{g)}	4.132 and 4.138 (merged s, 146.5, $=\text{CCH}_2\text{Br}$), 4.244, 4.250 and 4.256 (merged s, 99.2, $=\text{CCH}_2\text{Cl}$)
4	Br ₂	1:5	82	3d (37) 3e (100) 3f (40)	4.135 (s, 89.7, $=\text{CCH}_2\text{Br}$), 4.246 (s, 30.6, $=\text{CCH}_2\text{Cl}$)

a) For each run 0.5 g of **1** was used. b) Determined by GC. c) Determined by GCMS.
 d) Data of the product mixture recorded on a 200 MHz instrument in CDCl₃. e) Peak area.
 f) Distribution of the product mixture after it was subjected to GC. g) Undesired products
 which decomposed during preparative GC experiment.

were easily removed by the treatment with hexane as insoluble material. In Run 1, a hexane miscible liquid, obtained after the work up of the reaction, was analyzed to be a mixture of tetrakis(chloromethyl)ethylene (**3a**), tris(chloromethyl)iodome-

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thylethylene (**1b**) and 1, 1, 2-tris(chloromethyl)-1-chloroprop-2-ene (**4**). A white solid obtained in Run 2 was analyzed to be a mixture of four tetrakis(halomethyl)-ethylene derivatives (**3c-f**). The reaction of **1** with bromine (Run 3) furnished a complex mixture which was found to be a mixture of tetrakis(halomethyl)ethylene derivatives (**3a, c-f**) accompanied by some undesired products arising from further addition of bromine to ethylene derivatives. In Run 4, a mixture comprising of three tetrakis(halomethyl)ethylene derivatives (**3d-f**) was obtained. All attempts to resolve these mixtures by column chromatography proved unsuccessful leaving no alternate other than the preparative gas chromatographic separation. The preparative gas chromatographic resolution of these mixtures was therefore attempted which also did not prove helpful due to an unprecedented phenomenon that these compounds undergo mutual halogen exchange under preparative gas chromatographic experimental conditions. The analysis was therefore made with the help of ^1H -NMR and GCMS data. To confirm this phenomenon, we subjected a mixture of **3** to preparative GC and the mixture collected. The comparative data of the two samples which is given in Table II clearly shows that these compounds undergo halogen exchange. The isomerization of **4** to **3a** during preparative GC experiments was also confirmed.

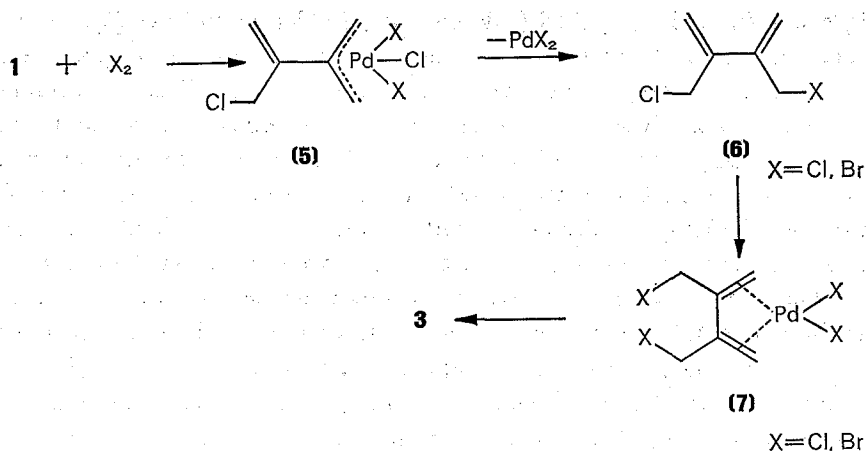
Table 2. GCMS Data of a Mixture of **3**

Compound	Initial composition (%)	Final ^{a)} composition (%)
3a	0	5
3c	13	15
3d	29	25
3e	43	29
3f	15	26

a) Conditions of preparative GC: injection temperature: 140°C, column temperature: 110°C, carrier gas: helium gas, column: Silicone OV-1(2%) (100X0.6 cm).

A plausible mechanism for these transformations may be outlined as in Scheme 1, in analogy to the mechanism proposed for the formation of tetrakis(bromomethyl)-ethylene (**1f**) by the reaction of π -allylpalladium complex (**2**) with bromine.⁹⁾ The addition of halogen to the palladium of **1** gives the Pd(IV) complex intermediate (**5**) which decomposes to furnish 1, 3-butadiene derivatives (**6**). The intermediate 1, 3-butadiene derivatives are then converted to tetrakis(halomethyl)ethylene derivatives (**3**) in the presence of liberated PdX_2 ($\text{X}=\text{Cl}, \text{Br}$).¹⁰⁾ The formation of **3b** can be explained by the simple addition of ICl to **6** ($\text{X}=\text{Cl}$). It is not clear why **4** dominated over **3a** in Run 1, while **4** readily isomerize to **3a** during preparative GC experiment.

In conclusion, the present manuscript reports the investigation of reaction of a π -allylpalladium complex (**1**) with iodine monochloride, iodine monobromide and bromine. Though the resolution of these reaction product is not possible, the use



Scheme 1

of these mixture, without further purification, for some cycloaddition and photocyclization reactions can not be ruled out. The reaction is interesting from the mechanistic point of view as it represents another example for the possible intermediacy of Pd (IV) complex. The palladium is recovered, almost quantitatively in the form of palladium (II) halides. The phenomenon of mutual halogen exchange during preparative GC experiments is also interesting.

EXPERIMENTAL

Reaction of 1 with Halogen/ Interhalogen; General Procedure. To a solution of **1** in chloroform was added halogen/interhalogen under argon atmosphere and the reaction mixture was left stirring 30 min at room temperature. The reaction mixture was then filtered, and the filtrate was washed successively with aqueous Na_2CO_3 , brine and water. The chloroform solution was then dried over $MgSO_4$ and the solvent evaporated.

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